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13. ABSTRACT (Maximum 200 words) The interactions of vibrationally excited HCl($v=2$) with MgO(100) surfaces have been examined in detail, with scattered HCl($v=2$) detected state selectively by resonance enhanced multiphoton ionization (REMPI). Simulations using a random walk model and "best estimates" for activation energies for desorption and hopping suggest that deactivation probably occurs at steps. In parallel, a new apparatus has been designed and built for a next generation of studies of molecular interactions on insulating oxide surfaces. Specifically, FTIR will be used to determine geometries and adsorption, and TPD, REMPI and other laser-based spectroscopies will be used to interrogate interactions of molecules and radicals with the surface and with other adsorbates.					
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**Final Report
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***DYNAMICS OF MOLECULE-SURFACE
INTERACTIONS ON METAL OXIDES***

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I. SUMMARY

The interactions of vibrationally excited $\text{HCl}(v=2)$ with $\text{MgO}(100)$ surfaces have been examined in detail, with scattered $\text{HCl}(v=2)$ detected state selectively by resonance enhanced multiphoton ionization (REMPI). In parallel, a new apparatus has been designed and built for a next generation of studies of molecular interactions on insulating surfaces. With the new apparatus, we are able to study the geometries and interactions of molecules adsorbed on insulator oxide surfaces. Below, we summarize our findings with $\text{HCl}(v=2)$ and describe the new apparatus.

II. ACCOMPLISHMENTS

II.1. $\text{HCl}(v=2)$ on $\text{MgO}(100)$

Following our studies of $\text{HCl}(v=0)$ scattering from $\text{MgO}(100)$, $\text{HCl}(v=2)$ was examined. Previous work has shown that molecules such as water and HCl do not chemisorb on $\text{MgO}(100)$ terraces, even at incident energies up to ~ 1 eV. On the other hand, MgO powders are known to be acid-base catalysts that react with such molecules at high temperatures and pressures. Thus, we set out to answer questions such as: Would vibrational excitation promote reaction with the surface? Would vibrational excitation survive impact with the surface? What are the energy transfer mechanisms?

The experiments required efficient photoexcitation of incident HCl to $v=2$. This was achieved by using a custom-built parametric oscillator (OPO) with 300 MHz linewidth and active frequency stabilization (Laser Vision). Output of 4 mJ was sufficient to saturate the $2 \leftarrow 0$ overtone, and the frequency could be held at an absorption line center indefinitely, e.g., one experiment lasted 36 hours. This remarkable device made the experiments possible.

It was found that $\text{HCl}(v=2)$ did not react on MgO terraces. Rather, at $T_s = 300$ K and incident energies of 0.1 – 0.9 eV, the scattered molecules retained their $v=2$ excitation. At the higher collision energies, the rotational, translational, and angular distributions of scattered $v=2$ molecules displayed the signatures of direct inelastic scattering. However, at 0.11 eV and $T_s = 120$ - 300 K they did not. The $v=2$ rotational and translational energies were accommodated at T_s . For $T_s > 160$ K, the $v=2$ excitation was not significantly quenched; most of the incident $v=2$ survived trapping-desorption with its vibrational excitation intact. Since MgO is an insulator and its phonon frequencies are much smaller than the HCl frequency, inefficient deactivation was not too surprising. As T_s was lowered, the desorption rate decreased, and the $v=2$ signal also decreased — by an order of magnitude between 160 and 120 K.

The TOF distributions were more surprising. In our study of $\text{HCl}(v=0)$ trapping-desorption, surface residence times > 1 ms were found for $T_s < 180$ K. Thus, we expected that as T_s was lowered, the TOF distributions would broaden and exhibit time profiles longer than those of the $v=2$ segment of the incident molecular beam (i.e., the OPO "optical chopper" provided 1 μs resolution). However, the time profiles of the incident and scattered beams tracked one another under all conditions, even at the lowest T_s (120 K). This is clearly due to an interplay between the vibrational deactivation and desorption rates. Simulations using a random walk model and "best estimates" for activation energies for desorption and hopping suggest that deactivation probably occurs at steps.

We propose the following mechanism. $\text{HCl}(v=2)$ roams the terrace via a two-dimensional random walk until it either desorbs with $v=2$ intact or reaches a step, where it is deactivated more efficiently than on terrace sites. According to this model, the residence time of $\text{HCl}(v=2)$ on terrace sites is long, possibly longer than 1 μs , and the probability of encountering a step increases as T_s decreases because of the increased diffusion time. Our surfaces are prepared such that there are minimal oxygen deficiencies. However, with cleaved surfaces steps are always present. According to our simulations, at low T_s the average distance that molecules diffuse from their landing site exceeds the average distance between steps (several hundred Å). Thus the excited molecules reach the steps.

This admittedly crude model rationalizes how the time behavior and signal intensity change with T_s . The observation of a small $v=1$ signal also supports this mechanism. Independent of the details of the mechanism, the result that $v=2$ excitation is retained long enough for its other degrees of freedom to be equilibrated at T_s is robust, and opens the way to new investigations of molecules with high levels of vibrational excitation.

II. 2. A new experimental arrangement for studies of interactions of excited molecules and radicals with surfaces

In parallel with the work on $\text{HCl}(v=2)$, the design and construction of the next generation UHV apparatus for studies of reactivity of excited molecules and radicals at interfaces was completed. This new machine, with its increased capabilities, constitutes a qualitative improvement over our previous arrangement. The new apparatus features FTIR, TOF and REMPI spectroscopies, as well as the capability of detecting H atoms using the high- n Rydberg TOF method.

The new experimental arrangement consists of a source chamber and a main interaction chamber. The main chamber features a three tier design: the top tier is designed to optimize

sensitivity for FTIR measurements of adsorbed species, the middle part includes traditional surface diagnostics such as Auger, XPS and LEED, and the bottom tier is dedicated to laser diagnostics of incident and scattered particles with well defined rovibrational and rotational excitations. The main design criteria were minimizing the distance between the pulsed nozzle and the interaction region (in order to maximize the incident flux), and incorporating additional diagnostics for surface adsorbates, particularly on insulators.

The source chamber is of rectangular shape, and includes two compartments, differentially pumped, separated by an orifice. The pulsed nozzle is mounted in the first compartment, with one or two skimmers attached to the wall separating the two compartments. The second compartment includes a chopper with its motor, designed to chop the $\sim 300 \mu\text{s}$ beam to 10-20 μs . This enables time-of-flight measurements with greater time resolution. The source chamber is separated from the main chamber by a sliding gate valve, which allows a quick change of nozzles without breaking vacuum in the main chamber. This is important especially for work with radicals. Despite the addition of the chopper compartment, we were able, through careful design, to keep the distance between the nozzle to the surface at 40 cm.

The laser beams enter the chamber from below, through a large window. The molecular beam hits the surface in the bottom tier, which includes also mass spectrometers for monitoring the incident and scattered beams for TPD measurements. Laser measurements in this tier include: (i) REMPI determination of internal states of scattered products; (ii) time-of-flight distributions obtained by changing the time delay between the opening of the nozzle and firing of the probe laser, or between the firing of the pump laser used to excite the incident molecules and the probe; and (iii) determination of angular distributions by rotating the surface in the scattering plane. He-diffraction is also carried out in this tier.

The second tier includes traditional surface diagnostics such as LEED, Auger, etc. Dosing of the surface can be done in this tier. It will be used principally to characterize the surface before and after the experiment, in order to avoid crowding in the area of the laser experiments.

The top tier, separated from the second by a gate valve, is designed to optimize FTIR detection sensitivity for adsorbates by minimizing the path of the IR beam. We have also worked with the FTIR manufacturer (Nicolet) to maximize the sensitivity of our detector (InSb) by including, for example, cold and warm filters for enhanced sensitivity in the frequency range suitable for detection of OH(D) and HCl vibrations ($2,500\text{--}4,000 \text{ cm}^{-1}$). We believe that the combination of a short beam path and efficient detector design will yield performance superior to other FTIR-surface arrangements.

The main challenge was to reach the three tiers of the UHV chamber with a long manipulator carrying the crystal holder with cooling (to 80 K) and heating (to 1000 K) capabilities. For this design, we turned to VG Instruments, a company with a sustained excellent track record in manufacturing long manipulators. They were represented in the US by the Kurt Lesker Company which was charged with the design of the crystal holder system. We worked closely with VG Instruments and the Kurt Lesker Company to minimize wobble, maximize pointing stability, enable both cooling and heating, and move freely between tiers. Unfortunately, we discovered after we received the manipulator that the crystal holder design was totally inadequate, and that VG fired the Kurt Lesker company as their representative. For example, the "CryoTiger", which was supposed to deliver closed-loop refrigeration, was unable to provide the specified temperature of 80 K. It was replaced with a Helium refrigerator, but this design was also found inadequate. After several unsuccessful attempts, the crystal holder and the heating/cooling systems were completely redesigned and rebuilt by us. We are finally able to reach the required temperature of 80 K, and heat at the rate of 3 K s^{-1} , necessary for TPD. After a stressful delay of several months, the instrument is fully operational, and we have obtained TPD curves of water on MgO(100), as well as preliminary signals with the FTIR spectrometer.

III. PERSONNEL

Mikhail Korolik — graduate student, now at Silicon Genesis Corporation

Minda Suchan - graduate student, supported partly by Dean and Dissertation Fellowships

Wousik Kim - postdoc; Ph.D. from UCLA

Samantha Hawkins - supported partly by a Dean's Fellowship

George Kumi - supported partly by a Merit Fellowship

IV. PUBLICATIONS

The effect of translational energy on collision-induced dissociation of highly excited NO_2 on MgO(100), D.W. Arnold, M. Korolik, C. Wittig and H. Reisler, *Chem. Phys. Lett.* **282**, 313 (1998).

Trapping-desorption and direct-inelastic scattering of HCl from MgO(100), M. Korolik, D.W. Arnold, M.J. Johnson, M.M. Suchan H. Reisler, and C. Wittig, *Chem. Phys. Lett.* **284**, 164 (1998).

Survival of $\text{HCl}(v=2)$ in trapping-desorption from MgO(100), M. Korolik, M. M. Suchan, M. J. Johnson, D. W. Arnold, H. Reisler, and C. Wittig, *Chem. Phys. Lett.*, **326**, 11-21 (2000).

V. INTERACTIONS/TRANSITIONS

PRESENTATIONS AT MEETINGS

1. "Scattering of HCl ($v = 0$) from MgO (100)" M. Suchan, M. Korolik, D.W. Arnold, M.J. Johnson, H. Reisler and Curt Wittig, presented by Minda Suchan at the USC Graduate Research Symposium, Lake Arrowhead, Sept., 1998.
2. "Survival of HCl($v=2$) in trapping-desorption from MgO(100)", presented by Wousik Kim at the Gordon Research Conference on Surface Dynamics, Summer, 1999.
3. "Survival of HCl($v=2$) in trapping-desorption from MgO(100)", presented by Minda Suchan at the USC Graduate Research Symposium, Catalina Island, Sept., 1999.
4. "Survival of HCl($v=2$) in trapping-desorption from MgO(100)", M. Korolik, M. M. Suchan, M. J. Johnson, D. W. Arnold, H. Reisler, and C. Wittig, to be presented in "Excited States at Surfaces" Faraday Discussion 117, University of Nottingham, UK, September, 2000.

VI. HONORS/AWARDS

1. Wousik Kim was awarded the UCLA Thesis Award
2. Minda Suchan got a USC Research Award for her presentation: "Scattering of HCl ($v = 2$) from MgO (100)", April 1998.
3. Minda Suchan got a USC Dissertation Award for her thesis work funded by AFOSR.